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(54)【発明の名称】 中性子遮蔽材用組成物、遮蔽材、容器

(57)【要約】

【課題】 高燃焼度対応の使用済核燃料貯蔵時の高温下でも耐熱性を有し、中性子遮蔽能力を確保した中性子遮蔽材料を提供すること。

【解決手段】 重合開始剤と、重合成分と、ホウ素化合物とを含む中性子遮蔽材用組成物により、アミン系硬化剤を用いないことで耐熱性を向上させ、且つ中性子遮蔽能力を確保した中性子遮蔽材を提供する。本発明の重合成分として、特にエポキシ成分とオキセタン成分が好ましく用いられる。

で、使用済核燃料の貯蔵目安である約60年間耐えうることが望ましい。

【0004】このため、遮蔽材としては水素密度の高い物質、特に水の使用が提案され、一部実用にも供されている。しかし、水は液体であるため、取り扱いが困難で、特に輸送と貯蔵を目的とするキャスクには適さない。また、100°C以上に達するキャスク内で沸騰をおさえるのが困難であるという問題がある。

【0005】従来、中性子遮蔽材の一材料として樹脂組成物が用いられ、その樹脂組成物の1つにエポキシ樹脂が用いられてきた。一般的に、樹脂組成物の水素含有量と耐熱性とは相反関係にあり、水素含有量が多いものは耐熱性が低く、耐熱性が高いものは水素含有量が低い傾向にある。エポキシ樹脂は、耐熱性や硬化性には優れるものの、中性子を減速させるために必要な水素の含有量が少ないとする傾向にあるため、これを水素含有量が多いアミン系の硬化剤で補う方法が一般的であった。

【0006】特開平6-148388号公報には、多官能アミン系エポキシ樹脂を用い、粘度を低下させて常温での作業性を向上させるとともに、ボットライフに優れた中性子遮蔽材用組成物が開示されている。また、特開平9-176496号公報には、アクリル樹脂、エポキシ樹脂、シリコーン樹脂等からなる組成物をポリアミン系の硬化剤で硬化させた中性子遮蔽材が開示されている。

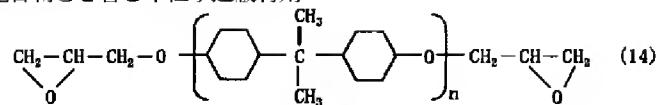
【0007】アミン系化合物は比較的水素含有量が多いため、中性子の吸収効果は向上するが、アミン系硬化剤に含まれる炭素と窒素の結合は熱により分解し易い。従って、従来のアミン系の硬化剤により硬化した樹脂からなる中性子遮蔽材よりも、新しい高燃焼度対応の使用済核燃料を貯蔵し保管するために必要な耐久性を有する組成物の開発が望まれる。

【0008】

【発明が解決する課題】本発明は、従来の組成物に比べて、熱耐久性がより向上し、かつ、中性子の吸収を確保した中性子遮蔽材用組成物を提供することを目的とする。

【0009】

【課題を解決するための手段】本発明は、重合開始剤と、重合成分と、ホウ素化合物とを含む中性子遮蔽材用*

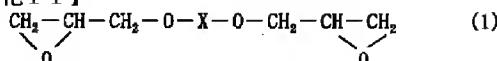


(構造式(14)中、n=1~3)を含むことが好ましい。また、前記エポキシ成分が、

【化14】

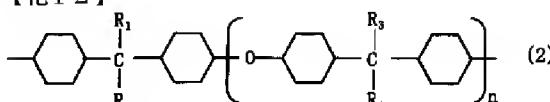
*組成物を提供する。本発明は、硬化剤を含まない中性子遮蔽材用組成物を提供するものである。重合成分としては、エポキシ成分を含むことが好ましい。また、エポキシ成分として、特に水素添加型エポキシ化合物を含むことが好ましい。ここで、水素添加型エポキシ化合物とは、ベンゼン環の少なくとも一部に水素を添加して、ベンゼン環の一部の共役状態を壊しつつも、環状構造を維持して水素の含有量を高めたエポキシ化合物をいう。また、本発明は、

10 【化11】

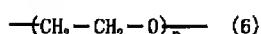
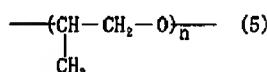
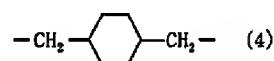
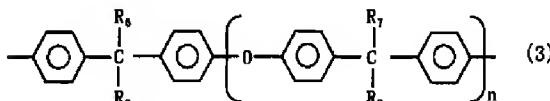


(構造式(1)中、Xは、

【化12】

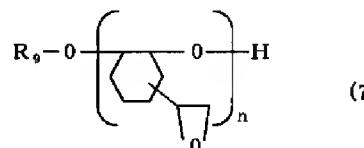


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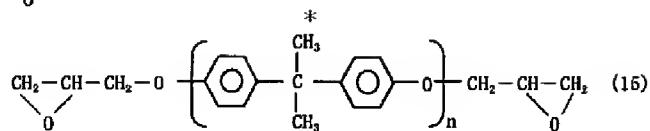
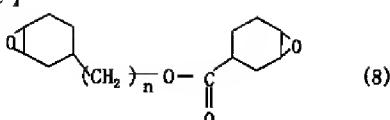
(構造式(2)中、R₁~R₄は、それぞれ独立して、C₃H₅、H、F、C₁、Brからなる群から選択され、n=0~2であり、構造式(3)中、R₅~R₈は、それぞれ独立して、CH₃、H、F、C₁、Brからなる群から選択され、n=0~2であり、構造式(5)中、n=1~12であり、構造式(6)中、n=1~24である)のいずれか、あるいは、Cが1~20のアルキル基から選択される1以上の化合物である)を含むことが好ましい。前記エポキシ成分が、

【化13】



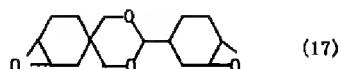
(構造式(7)中、R₉はCが1~10のアルキル基、50 またはHであり、n=1~24)と、

【化15】



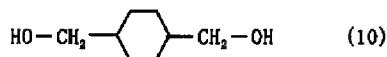
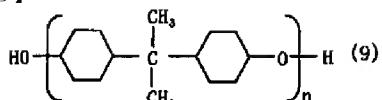
(構造式(15)中n=1~3)と、

【化17】



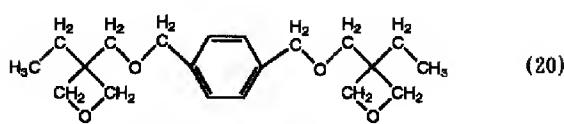
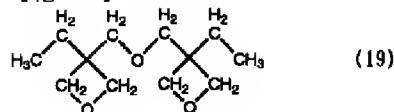
とからなる群から選択される1つ以上の化合物を含むことが好ましい。さらに本発明の中性子遮蔽材用組成物は、該組成物の水素含有量を増加させる化合物をさらに含むことが好ましく、前記水素含有量を増加させる化合物として、

【化18】



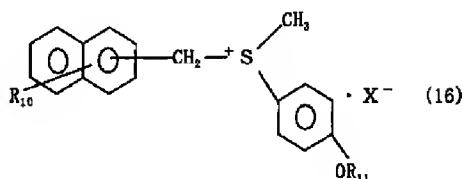
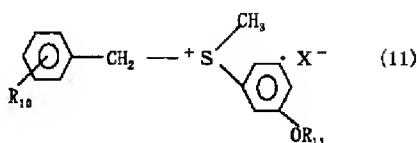
(構造式(9)中、n=1~3)の少なくとも1種以上を含むことが好ましい。重合成分としてオキセタン化合物を含むことが好ましく、オキセタン化合物が、

【化19】



のうち、少なくとも1種以上を含むことが好ましい。さらに、前記重合開始剤が、カチオン重合開始剤を含むことが好ましく、前記カチオン重合開始剤が、

【化20】

* (構造式(8)中n=1~8)と、
【化16】

(構造式(11)、構造式(16)中、R₁₀は、水素原子、ハロゲン原子、ニトロ基、メチル基であり、R₁₁は、水素原子、CH₃CO、CH₃OOC、XはSbF₆、PF₆、BF₄、AsF₆である)を含むことが好ましい。また、充填剤をさらに含むことが好ましく、耐火材をさらに含むことが好ましく、前記耐火材が、水酸化マグネシウム、水酸化アルミニウムの少なくとも1種以上を含むことが好ましい。本発明はさらに、中性子遮蔽材用組成物により製造された中性子遮蔽材および中性子遮蔽容器を提供する。本発明の組成物は、重合開始剤により重合可能な化合物、好ましくはエポキシ成分と重合開始剤とにより反応が進行し、熱に弱いアミン系の硬化剤を含まないため、本発明の組成物を材料とするキャスクは耐熱性が向上したものとなっている。また、組成物中の水素含有量も基準値を満足しており、中性子の遮蔽性能も確保している。

【0010】

【発明の実施の態様】以下に、本発明の実施の態様を詳細に説明する。なお、以下に説明する実施の態様は、本発明を限定するものではない。本発明を通じて、重合成分とは、重合開始剤によって重合可能な化合物をいう。特には、本発明においては、以下のエポキシ成分とオキセタン成分を重合成分として含む。エポキシ成分とは、エポキシ環を有する化合物（以下、エポキシ化合物といふ）をいい、一種類のエポキシ化合物である場合も、二種類以上のエポキシ化合物の混合物である場合も含む。同様にオキセタン環を有する化合物をオキセタン化合物といい、一種類のオキセタン化合物である場合も、二種類以上のオキセタン化合物の混合物である場合も含む。樹脂成分とは、以上のような重合成分と重合開始剤成分

とをあわせたもの、及びこれらに水素含有量を増加させる化合物、例えばジオール等をあわせたものをいう。

【0011】本発明では、カチオン重合可能な化合物、特には、エポキシ化合物またはオキセタン化合物あるいはそれらの両方に重合開始剤成分を添加することにより、熱に弱いアミン部分を持つ硬化剤を使用せずに硬化させることを可能とする。従来の組成物は、硬化剤にアミン化合物を用いるために耐熱性、特に長期高温状態での耐熱分解性が低下した。本発明では、このような硬化剤を使用することなく硬化を可能とすることで、高温状態で結合が分解しやすい炭素と窒素の結合部分が存在しない樹脂を得ることができ、大きな耐熱性が期待できる。従って、従来のような硬化剤使用に伴う耐熱性低下がないため、重合成分の選択で水素添加量、耐熱性といった所望の性質を付加しうるという利点がある。

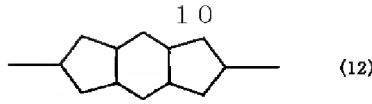
【0012】本発明は、重合成分と、重合開始剤成分と、中性子吸収剤であるホウ素化合物と、耐火材とを含んでなる組成物であり、硬化させて樹脂としたときに、耐熱性に優れ、高い中性子遮蔽効果を有することを特徴とする水素含有率が高い組成物である。具体的には、本発明の組成物には、硬化物の熱重量分析による重量残存率90重量%の温度が330°C以上、好ましくは350°C以上、樹脂成分全体に占める水素含有量が好ましくは9.0重量%以上、さらに好ましくは9.8重量%以上であることが求められる。これは、水素含有量が9.0重量%以上であれば、耐火材充填量の調整等で目的とする中性子遮蔽効果の確保を期待できるためである。

【0013】又、これに加えて更に詳細には、長期間高温密閉環境下での熱耐久後の硬化物の重量減少及び圧縮強度の低下が小さい程良く、例えば190°C×1000hrの密閉熱耐久後の重量減少率は0.5重量%以下、好ましくは0.2重量%以下、圧縮強度は低下していないか、最も好ましくはむしろ上昇傾向にあることが求められる。

【0014】本発明の重合成分には、耐熱性の高い化合物を用いることが好ましい。特に、100°C以上、好ましくは200°C付近における耐熱性が必要であるという観点から、エポキシ化合物が好ましく用いられる。

【0015】本発明のエポキシ成分には、カチオン系の重合開始剤成分を用いて重合することができるエポキシ環を有する化合物を用いる。耐熱性を向上させるためには、エポキシ成分の架橋密度が高いことが好ましい。また、環構造を多く含むと強固な構造となるため、耐熱性を向上させることができる。環構造には、例えば、ベンゼン環が挙げられる。ベンゼン環は剛直で耐熱性にはすぐれているが、本発明において中性子を減速する役割をもつ水素の含有量が少ないため、ベンゼン環に水素付加した化合物がさらに好ましい。耐熱性の高い剛直な構造としては、

【化21】



で示される構造が好ましい。水素をより多く含有することが好ましいため、

【化22】



で示される構造が最も好ましい。このような、ベンゼン

10 環に水素を添加した環構造を有するエポキシ化合物は、本明細書を通じて、水素添加型エポキシ化合物という。水素添加型エポキシ化合物は、耐熱性のある構造を有し、水素含有率が高いことから、本発明のエポキシ化合物として最も好ましい。

【0016】エポキシ成分は、一種類のエポキシ化合物でも、複数のエポキシ化合物を混合したものであってもよい。耐熱性、水素含有量增加といった所望の性能を付与することができるようエポキシ化合物を選択する。

【0017】これらのエポキシ成分の組成は、樹脂成分の水素含有量が中性子を遮蔽するのに十分な量、好ましくは9.0重量%以上、さらに好ましくは9.8重量%以上になるように決定する。中性子遮蔽材の中性子遮蔽性能は中性子遮蔽材の水素含有量（密度）と中性子遮蔽材の厚さにより決定される。この値は、キャスクに求められる中性子遮蔽性能とキャスクの中性子遮蔽材の設計厚さから決定される中性子遮蔽材に要求される水素含有量（密度）をもとに、中性子遮蔽材に混練される耐火材や中性子吸収材の配合量を考慮して樹脂成分に求められる水素含有量を算出した値を基準にしたものである。

【0018】このような観点から、エポキシ環を好ましくは複数有する化合物であって、剛直な構造、または構造式(12)または構造式(13)で表されるような環構造を有し、かつ水素含有量が多い化合物が、本発明のエポキシ成分として適切である。このようなエポキシ成分は、一般に構造式(1)で表され、式中Xは、構造式(2)（式中R₁～R₄は、それぞれ独立して、CH₃、H、F、Cl、Brから選択され、n=0～2である）、構造式(3)（式中R₅～R₈は、それぞれ独立して、CH₃、H、F、Cl、Brから選択され、n=0～2である）、構造式(4)、構造式(5)（式中、n=1～12）、構造式(6)（式中、n=1～24）から選択されることが好ましい。

【0019】中でも、水素含有量と耐熱性のバランスから、構造式(14)で表される水素添加ビスフェノールA型エポキシが、最も好適かつ重要なエポキシ成分として用いられる。

【0020】さらに耐熱性を付与するための成分として、ビスフェノールA型エポキシ（構造式(15)）を添加することができる。ベンゼン環を有し、剛直な構造を有するからである。また、架橋密度が高く、耐熱性が

良好であるといった観点からは、構造式(7)（式中、R₉はCが1～10のアルキル基、またはHであり、n=1～24）、構造式(8)（式中、n=1～8）、または構造式(17)を添加することが好ましい。

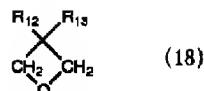
【0021】従って、例えば構造式(14)に、構造式(15)、構造式(7)、構造式(8)、構造式(17)からなる群から選択される少なくとも1以上の化合物を混合して用いることにより、所望の水素含有量および耐熱性を有する組成物とすることが可能となる。したがって、本発明のエポキシ成分は、構造式(14)で示されるエポキシ化合物を含み、さらに、構造式(15)、構造式(7)、構造式(8)、構造式(17)の全てを含んでもよく、それらのうちの一部を含んでもよい。これらのエポキシ化合物を用いて、考えられる全ての組み合わせが可能である。

【0022】この場合、樹脂成分全体に対し、構造式(14)の水素添加ビスフェノールA型エポキシを70重量%以上含むことが好ましく、構造式(15)のビスA型エポキシは20重量%以下、構造式(7)は30重量%以下、構造式(8)は25重量%以下、構造式(17)は30重量%以下の量で含むことが好ましい。

【0023】また、重合成分として、特に水素添加量を増大させる観点からはオキセタン化合物を用いることができる。オキセタン化合物は、エポキシと同様にカチオン重合が可能であり、水素含有量が豊富で且つ、耐熱性もある程度期待できる。

【0024】オキセタン化合物は、一般的に、構造式(18)

【化23】



(構造式(18)中、R₁₂、R₁₃はそれぞれ独立して、H、ハロゲン、Cが1～8のアルキル、アルコール、その他の炭素と水素と酸素とからなる有機化合物を含む構造である)で表される。本発明で用いられるオキセタン化合物は、エーテル結合やベンゼン環を介して二つ以上のオキセタン環を有する化合物であってもよい。

【0025】本発明に使用するオキセタン化合物とし

て、具体的には、構造式(19)、構造式(20)が好ましい。また、これらに限定されるものではなく、構造式(19)と同様に、例えばエーテル結合や環構造等を介して少なくとも二つ以上のオキセタン環を有する化合物が好ましい。オキセタン環を多く含むことで、架橋密度の向上による耐熱性の付与が期待できるためである。また、本発明の組成物には、特に耐熱性の付与が求められるため、環構造、分枝構造等を多く有するオキセタン化合物が好ましい。

10 【0026】オキセタン成分は、重合成分として、エポキシ化合物を使用することなく単独で用いることもできる。2つ以上のオキセタン化合物を用いることもできる。また任意のエポキシ成分と併用した重合成分として用いることができる。例えば、好ましい重合成分の組み合わせとしては、構造式(19)のオキセタン成分と構造式(7)のエポキシ成分、構造式(19)のオキセタン成分と構造式(8)のエポキシ成分、構造式(19)のオキセタン成分と構造式(17)のエポキシ成分などを用いることが可能である。

20 【0027】オキセタン化合物を用いた重合成分の組成比の一例としては、構造式(19)を85.5重量%と構造式(15)を14.5%含むものが挙げられる。また、構造式(19)を74.0重量%と構造式(20)を20.0重量%と構造式(7)を6.0%含むものが挙げられる。

【0028】重合開始剤としては、ラジカル系、アニオン系、カチオン系等に分類されそれぞれ文献等で多数報告されているが、本発明では、カチオン系の重合開始剤が好ましく用いられる。カチオン系の重合開始剤として

30 著名なものの一例を表1に示す。また、熱で重合を開始させることができるカチオン系熱重合開始剤としては旭電化工業(株)のオプトンCPシリーズや三新化学(株)のSIシリーズ、ダイセル化学工業(株)のDATICATEX-1等が挙げられる。本発明ではこれらの重合開始剤を用いることが可能であるが、それらには限定されない。

【0029】

【表1】

13
一般的な重合開始剤成分

14

構造	商品名	供給元
	X=SbF6 UVI-6974	UCC
	X=PF6 UVI-6990	UCC
	X=SbF6 UVI-6970 (SP-170) X=PF6 UVI-6950 (SP-150)	旭電化
	Degacure K126	Degussa
	FX-512	3M
	X=SbF6 PIC-061T X=PF6 PIC-062T	日本化薬
	X=SbF6 PIC-020T X=PF6 PIC-022T	日本化薬
	合成スルホニウム塗	日本曹達
	UV-9380C	GE
	IOC-10	GE
	CD-1012	Sartomer
	2074	Rhône-Poulenc Chimie
	Inuga-cure 261	Chiba-Geigy
		東芝

【0030】重合開始剤としては、好ましくは、構造式(11)または構造式(16)で示される化合物が添加される。重合開始剤は、樹脂成分全体を100重量部とした場合に、0.5~6重量部で添加することが好ましく、1~3重量部で添加するがさらに好ましい。あまり多く添加しすぎると、組成物全体に占める水素含有量を低下させることとなるおそれがあるからである。

【0031】さらに、本発明の組成物には、水素含有量を増加させるために、エポキシ環を有しない化合物であって、水素を多く含有する化合物を添加することも可能*50

*である。これらの化合物は、エポキシ化合物のみで水素含有量を増加するには限界があるため、水素含有量が不足する場合に、任意選択的に添加することができる。このとき、添加する化合物が組成物の系全体の物性を大きく変えることのないように化合物を選択する必要がある。例えば、本発明のカチオン系の重合開始剤を含む組成物に、アミン系の化合物を混合すると、エポキシ成分の重合反応が進行しないため、アミン系化合物を加えることはできない。このような点を考慮して検討した結果、水素含有量を増加させるための化合物としては、例

えば、ジオール類が適している。

【0032】ジオール類としては、エポキシ成分に可溶で且つエポキシ成分と重合可能であるものであれば適用可能であり、脂肪族ジオール、芳香族ジオール、脂環構造を有するジオール、ポリオールなどを使用することが出来るが、これらに限定されない。水素含有量の増加と耐熱性低下の抑制の点からは、好ましくは脂環構造を有するジオール、例えば構造式(9)、構造式(10)で表される化合物を使用する。ジオール類の添加量は、樹脂成分全体に対して、30重量%以下であることが好ましく、20重量%以下であることがさらに好ましい。

【0033】組成物の水素含有量を増加させるための化合物としては、ジオール類に限定されず、カチオン硬化が可能なオキセタン類やビニルエーテル類、及びジオール類と同様の効果を期待できる物として3官能以上の多官能型のアルコール類などを用いることも可能である。

【0034】本発明の組成物の中性子吸収剤として使用されるホウ素化合物には、炭化ホウ素、窒化ホウ素、無水ホウ酸、ホウ素鉄、灰ホウ石、正ホウ酸、メタホウ酸等があるが、中性子遮蔽性能の点で炭化ホウ素が最も好ましい。

【0035】上記のホウ素化合物は、粉末が用いられるがその粒度及び添加量には特に制限はない。しかし、マトリックス樹脂のエポキシ樹脂内の分散性、中性子に対する遮蔽性を考慮すれば平均粒径は1～200ミクロン程度が好ましく、10～100ミクロン程度がより好ましく、20～50ミクロン程度が特に好ましい。一方、添加量は後述の充填剤も含めた組成物全体に対して0.5ないし20重量%の範囲が最も好ましい。0.5重量%未満では加えたホウ素化合物の中性子遮蔽材としての効果が低く、また、20重量%を超えた場合はホウ素化合物を均一に分散させることが困難になる。

【0036】本発明には充填剤として、シリカ、アルミニナ、炭酸カルシウム、三酸化アンチモン、酸化チタン、アスベスト、クレー、マイカ等の粉末の他、ガラス纖維等も用いられ、また、必要に応じ炭素纖維等を添加しても良い。更に必要に応じて、離型剤としての天然ワックス、脂肪酸の金属塩、酸アミド類、脂肪酸エステル類等、難燃剤としての塩化パラフィン、ブロムトルエン、ヘキサブロムベンゼン、三酸化アンチモン等、着色剤としてのカーボンブラック、ベンガラ等の他、シランカップリング剤、チタンカップリング剤等を添加することができる。

【0037】本発明に係る組成物において使用される耐火剤は、万一、火災に遭遇した場合でも、ある程度以上の中性子遮蔽能力を維持できるよう、中性子遮蔽材をある程度以上残存させることを目的としている。このような耐火材としては、特に、水酸化マグネシウム、水酸化アルミニウムを使用することが好ましい。中でも、水酸化マグネシウムは200℃近い高温でも安定に存在する

ため、特に好ましい。これら耐火剤の添加量は上記組成物全体中20～70重量%が好ましく、35～60重量%が特に好ましい。

【0038】本発明の組成物は、重合成分、例えばエポキシ成分とその他の添加剤とを混合後して樹脂組成物を調製し、これと耐火材や中性子吸収材等を混練した後、最後に重合開始剤を添加することによって調整する。重合条件としては、樹脂成分の組成によても異なるが、50℃～200℃の温度条件において、1時間～3時間10加熱を行うことが好ましい。さらには、このような加熱処理は2段階で行なうことが好ましく、80℃～120℃で1時間～2時間加熱した後、120℃～180℃で、2時間から3時間加熱処理することが好ましいが、調製方法や硬化条件等これに限定されるものではない。

【0039】さらには、使用済核燃料の中性子を効果的に遮蔽して貯蔵・輸送するための容器、好ましくはキャスクを製造することができる。このような輸送用のキャスクは、公知技術を利用して製造することができる。例えば、特開平2000-9890号公報に開示されたキャスクにおいて、中性子遮蔽体を充填する個所が設けられている。このような個所に、本発明の組成物を充填することができる。

【0040】このようなキャスク中の遮蔽体に限定されることなく、本発明の組成物は、中性子の拡散を防止する装置や施設において、さまざまな個所に用いることができ、効果的に中性子を遮蔽することができる。

【0041】

【実施例】以下に、実施例を用いて本発明を詳細に説明する。なお、以下の実施例は本発明を限定するものではない。

【0042】実施例において、本発明の組成物を調製し、中性子遮蔽効果を調べた。通常は中性子遮蔽材用樹脂組成物に、耐火材として水酸化アルミニウムや水酸化マグネシウム等を全体の60重量%程度、及び中性子吸収剤として炭化ホウ素等のホウ素化合物を全体の1重量%程度を混合して、中性子遮蔽材を作製する。しかし、ここでは樹脂成分、即ち、重合成分と重合開始剤成分等による性能を評価すべく耐火材および中性子吸収剤は添加しないものを中心とした。

【0043】中性子遮蔽材に求められる性能としては、耐熱性（重量残存率、圧縮強度等）、耐火性、水素含有量（中性子遮蔽としての適性の判断目安として材料中の水素含有密度がある一定量以上あることが必要となる）等がある。耐火性は耐火材による部分が大であるため、中性子遮蔽材用樹脂組成物の評価としては重量残存率に見る耐熱性と水素含有量を評価した。重量残存率は、昇温時の重量変化を測定することにより、その耐熱性を評価するものである。測定にはTGAを用い、熱重量減少の測定条件は室温～600℃までを昇温速度10°C/min、窒素雰囲気下にて測定した。また、樹脂に求められる水素

含有量の基準値としては樹脂単体中での水素含有量を9.8重量%程度以上とした。

【0044】〔実施例1〕エポキシ樹脂として、水素添加ビスフェノールA型エポキシ樹脂（油化シェルエポキシ（株）製、YL6663、構造式（14））100gに、カチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。上記中性子遮蔽材用樹脂組成物の水素含有量を測定した結果、水素含有量は9.8重量%以上（10重量%程度以上）で基準値を満足した。次に、組成物を80°C×30min+150°C×2hrで硬化させ、その硬化物の熱重量減少をTGAにより測定した。熱重量減少の測定条件はRT～600°Cまでを昇温速度10°C/min、窒素雰囲気下にて測定した。測定の結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が350°C以上と極めて良好な耐熱性、熱安定性を示した。

【0045】〔実施例2〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂（YL6663、構造式（14））84.6gと、ビスフェノールA型エポキシ樹脂（油化シェルエポキシ（株）製、エピコート828、構造式（15））15.4gを混合した後にカチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。実施例1と同様の方法にて樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が380°C以上と極めて良好な耐熱性、熱安定性を示した。

【0046】〔実施例3〕エポキシ樹脂として、水素添加ビスフェノールA型エポキシ樹脂（YL6663、構造式（14））74.8g、多官能脂環型エポキシ樹脂（ダイセル化学（株）製、EHPE3150、構造式（7））25.2gを混合し、110°Cに保持してEHPE3150（固体）が溶解するまで良く攪拌した。EHPE3150溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が390°C以上と極めて良好な耐熱性、熱安定性を示した。

【0047】〔実施例4〕エポキシ樹脂として、水素添

加ビスフェノールA型エポキシ樹脂（YL6663、構造式（14））79.4gと、脂環型エポキシ樹脂（ダイセル化学（株）製、セロキサイド2021P、構造式（8））20.6gを混合したものにカチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が370°C以上と極めて良好な耐熱性、熱安定性を示した。

【0048】〔実施例5〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂（YL6663、構造式（14））8.23gとビスフェノールA型エポキシ樹脂（エピコート828、構造式（15））8.85gと、脂環型エポキシ樹脂（セロキサイド2021P、構造式（8））8.85gを混合した後にカチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が380°C以上と極めて良好な耐熱性、熱安定性を示した。

【0049】〔実施例6〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂（YL6663、構造式（14））80.9gとビスフェノールA型エポキシ樹脂（エピコート828、構造式（15））9.55gと多官能脂環型エポキシ樹脂（EHPE3150、構造式（7））9.55gを混合し、110°Cに保持してEHPE3150（固体）が溶解するまで良く攪拌した。EHPE3150溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80（構造式（11））を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が390°C以上と極めて良好な耐熱性、熱安定性を示した。

【0050】〔実施例7〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂（YL6663、構造

式(14)) 77.3gと脂環型エポキシ樹脂(セロキサイド2021P、構造式(8)) 11.35gと多官能脂環型エポキシ樹脂(EHPE3150、構造式(7)) 11.35gを混合し、110℃に保持してEHPE3150(固体)が溶解するまで良く攪拌した。EHPE3150溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80(構造式(11))を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が390°C以上と極めて良好な耐熱性、熱安定性を示した。

【0051】〔実施例8〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂(YL6663、構造式(14)) 80.38gとビスフェノールA型エポキシ樹脂(エピコート828、構造式(15)) 6.54gと脂環型エポキシ樹脂(セロキサイド2021P、構造式(8)) 6.54gと多官能脂環型エポキシ樹脂(EHPE3150、構造式(7)) 6.54gを混合し、110℃に保持してEHPE3150(固体)が溶解するまで良く攪拌した。EHPE3150溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80(構造式(11))を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が400°C以上と極めて良好な耐熱性、熱安定性を示した。

【0052】〔実施例9〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂(YL6663、構造式(14)) 63.8gと、脂環型エポキシ樹脂(セロキサイド2021P、構造式(8)) 26.2gと、水添ビスフェノール(新日本理化(株)製、リカビノールHB、構造式(9))を10gを混合し、100℃に保持してリカビノールHB(固体)が溶解するまで良く攪拌した。リカビノールHB溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80(構造式(11))を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150

°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が380°C以上と極めて良好な耐熱性、熱安定性を示した。

【0053】〔実施例10〕エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂(YL6663、構造式(14)) 66.1gと脂環型エポキシ樹脂(セロキサイド2021P、構造式(8)) 23.9gと、シクロヘキサンジメタノール(東京化成工業(株)製、構造式(10)) 10gを混合し、100°Cに保持してシクロヘキサンジメタノール(ワックス状)が溶解するまで良く攪拌した。シクロヘキサンジメタノール溶解後室温に放置し、室温付近まで温度が低下したらカチオン系重合開始剤SI-80(構造式(11))を1g添加し、重合開始剤が溶解するまで良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%程度で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が380°C以上と極めて良好な耐熱性、熱安定性を示した。

【0054】〔実施例11〕ここでは、中性子吸収剤および耐熱材をさらに混合した中性子遮蔽材を評価した。エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂(YL6663、構造式(14)) 80.38gとビスフェノールA型エポキシ樹脂(エピコート828、構造式(15)) 6.54gと脂環型エポキシ樹脂(セロキサイド2021P、構造式(8)) 6.54gと多官能脂環型エポキシ樹脂(EHPE3150、構造式(7)) 6.54gを混合し、110°Cに保持してEHPE3150(固体)が溶解するまで良く攪拌した。EHPE3150溶解後、水酸化マグネシウムを146.5gと炭化ホウ素3.5gを混合・攪拌し170°C×2hr保持した。170°C×2hr保持後室温にて放置し、混合物の温度が室温程度にならカチオン系重合開始剤SI-80(構造式(11))を2g添加し良く攪拌して中性子遮蔽材用組成物とした。中性子遮蔽材に求められる水素含有量の目安としては、水素含有密度が0.096g/cm³以上である。調製した中性子遮蔽材組成物の水素含有密度を測定した結果、0.096g/cm³以上で基準値を満足した。又、別途測定した樹脂成分中の水素含有量は9.8重量%以上であった。一方、上記中性子遮蔽材用樹脂組成物を170°C×4hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以上、重量残存率90重量%の温度が400°C以上と極めて良好な耐熱性、熱安定性を示した。また、上記硬化物を密閉容器に封入後、190°C×1000hrの耐熱耐久試験を行った。圧縮強度は試験前に比べ1.4倍以上

上昇し、重量減少率も0.1%程度で極めて良好な耐久性を示した。

【0055】[実施例12]エポキシ樹脂として水素添加ビスフェノールA型エポキシ樹脂(YL6663、構造式(14))63.8gと脂環型エポキシ樹脂(セロキサイド2021P、構造式(8))26.2gと水添ビスフェノール(リカビノールHB、構造式(9))10.0gを混合し、100°Cに保持してリカビノールHB(固形)が溶解するまで良く攪拌した。リカビノールHB溶解後、水酸化マグネシウムを146.5gと炭化ホウ素3.5gを混合・攪拌し170°C×2hr保持した。170°C×2hr保持後室温にて放置し、混合物の温度が室温程度になつたらカチオン系重合開始剤S1-80L(構造式(11))を2g添加し良く攪拌して中性子遮蔽材用組成物とした。中性子遮蔽材に求められる水素含有量の目安としては、水素含有密度が0.096g/cm³以上であるが、調製した中性子遮蔽材組成物の水素含有密度を測定した結果、0.096g/cm³以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を170°C×4hrで硬化させ、熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が380°C以上と極めて良好な耐熱性、熱安定性を示した。また、上記硬化物を密閉容器に封入後、200°C×500hrの耐熱耐久試験を行つた。圧縮強度は試験前に比べ1.2倍以上も上昇し、重量減少率も0.1%程度で極めて良好な耐久性を示した。

【0056】次に比較例として、従来から用いられてきた組成物による中性子遮蔽材の性能を評価した。実施例と同様に、耐火材、中性子吸収剤は添加しなかつた。また、実施例と同様に、水素含有量は成分分析により、熱重量減少はTGAで測定することにより求めた。

【0057】[比較例1]エポキシ樹脂として実施例1と同様の構造式(14)で示される水素添加ビスフェノールA型エポキシ樹脂(油化シェルエポキシ(株)、YL6663)82.5gと、硬化剤としてイソホロンジアミン17.5gを良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。これは、本発明と比較した硬化剤を用いた中性子遮蔽材の比較例を示すものである。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が300°C程度であり、実施例の一群と比較して耐熱性、熱安定性が劣った。この組成系は実施例1と比較してカチオン系重合開始剤のかわりにアミン系硬化剤を使用する点が大きく異なつてゐる。実施例1と比較例1との比較から実施例1のように重合開始剤により硬化させることで耐熱性、熱安定性が向上

することがわかる。

【0058】[比較例2]エポキシ樹脂としてビスフェノールA型エポキシ樹脂(エピコート828、構造式(15))81.4gと、硬化剤としてイソホロンジアミン18.6gを良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は8.2重量%以下で基準値を大きく下回り未達となつた。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例

10 1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%程度、重量残存率90重量%の温度が350°C程度と耐熱性、熱安定性は良かった。この組成系は耐熱性、熱安定性的には良好だが、水素含有量の点から中性子遮蔽材用樹脂組成物としては不適であった。また、この組成系は比較例2と比較してカチオン系重合開始剤のかわりにアミン系硬化剤を使用する点が大きく異なつてゐる。比較例2と比較例3の比較からも、重合開始剤により硬化させることで耐熱性、熱安定性が向上することがわかる。

20 【0059】[比較例3]エポキシ樹脂としてビスフェノールA型エポキシ樹脂(エピコート828、構造式(15))とボリアミン系の硬化剤を1:1(化学量論的に等量となる)の割合で混合・攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99重量%以下、重量残存率90重量%の温度が300°C以下であり、実施例の一群と比較して耐熱性、熱安定性は劣つた。この組成系は従来から使用されている中性子遮蔽材用の樹脂組成物と同様の系を模擬したものだが、比較例4は水素含有量の点からは適性があるが、耐熱性、熱安定性的には実施例の一群と比較して低い値であり、実施例の一群が耐熱性、熱安定性に優れていることがわかる。

30 【0060】[比較例4]エポキシ樹脂としてポリプロピレングリコールの両末端のOHをそれぞれグリシジルエーテルに置換した構造を持つエポキシ樹脂(エポキシ40 等量190)81.7gと、硬化剤としてイソホロンジアミン18.3gを良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以下、重量残存率90重量%の温度が250°C程度未満であり、実施例の一群と比較して耐熱性、熱安定性が極めて劣つた。

50 【0061】[比較例5]エポキシ樹脂として1,6ヘ

キサンジグリシジルエーテル(エポキシ等量155)78.5gと、硬化剤としてイソホロンジアミン21.5gを良く攪拌して中性子遮蔽材用に用いる樹脂組成物とした。樹脂組成物中の水素含有量を測定した結果、水素含有量は9.8重量%以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99.5重量%以下、重量残存率90重量%の温度が300°C未満であり、実施例の一群と比較して耐熱性、熱安定性が劣った。

【0062】[比較例6]ここでは、従来型の樹脂成分に中性子吸収剤を添加して、中性子遮蔽効果を評価した。エポキシ樹脂としてビスフェノールA型エポキシ樹脂(エピコート828、構造式(15))50gとポリアミン系の硬化剤50gを混合・攪拌した後に水酸化マグネシウムを146.5gと炭化ホウ素3.5gを混合・攪拌して中性子遮蔽材用組成物とした。中性子遮蔽材に求められる水素含有量の目安としては、水素含有密度が0.096g/cm³以上であるが、調製した中性子遮蔽材組成物の水素含有密度を測定した結果、0.096g/cm³以上で基準値を満足した。一方、上記中性子遮蔽材用樹脂組成物を80°C×30min+150°C×2hrで硬化させ、実施例1と同様の方法にて熱重量減少を測定した結果、200°Cでの重量残存率99重量%以下、重量残

存率90重量%の温度が300°C以下であり、実施例の一群と比較して耐熱性、熱安定性は劣った。また、上記硬化物を密閉容器に封入後、190°C×1000hrの耐熱耐久試験を行った。圧縮強度は試験前に比べ3割以上低下し、高温環境下での耐久性は低いものとなった。この組成系は従来から使用されている中性子遮蔽材用組成物と同様の系を模擬したものだが、比較例6は水素含有量の点からは適性があるが、耐熱性、熱安定性的には実施例11及び実施例12と比較して低い値であり、実施例が耐熱性、熱安定性的に優れていることがわかる。

【0063】以上の、実施例、比較例から、同じ重合成分で比較したとき、アミン系硬化剤で硬化した樹脂に比べ、本発明の重合開始剤により硬化した樹脂では、重量残存率90重量%時点の温度が、平均して30~50°C上昇し耐熱性の高いものとなっていることがわかった。

【0064】

【発明の効果】本発明の中性子遮蔽材用組成物により得られた中性子遮蔽材は、カチオン系重合開始剤を用いて耐熱性のある重合成分を硬化させるものである。高温条件下で分解しやすい結合を有する硬化剤成分を用いることなく重合可能な本発明の組成物は、硬化して遮蔽剤としたときに、耐熱温度が上昇し、かつ中性子遮蔽効果も確保したものである。従って、本発明は使用済核燃料の長期にわたる貯蔵にも耐えることができる中性子遮蔽材用組成物を提供することができる。

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the constituent for neutron shielding materials. It is the material applied to the cask which are storage of spent reactor fuel and a container for conveyance, and is related with the constituent for neutron shielding materials which heat resistance improved and secured neutron cover nature.

[0002]

[Description of the Prior Art]The nuclear fuel used in nuclear installation, such as a nuclear power plant, is transported to a reprocessing plant, and reprocessing is usually presented with it. However, since the yield of such spent reactor fuel is over rework capability, the necessity of carrying out storage storage over a long period of time has produced spent reactor fuel now. Under the present circumstances, spent reactor fuel is paid and conveyed to the cask which is a neutron shield vessel, after being cooled by even radiation levels suitable for transportation, but emitting radiation, such as a neutron, also in this stage is being continued. Energy of a neutron is high, and since a gamma ray is generated and a serious injury is done to a human body, development of the material which covers this neutron certainly is needed.

[0003]Although it is known that a neutron will be absorbed by boron, in order for boron to absorb a neutron, it is necessary to slow down a neutron. It is known that hydrogen is the optimal as a substance for slowing down a neutron. Thus, many atoms of boron and hydrogen need to be included as a constituent for neutron shielding materials. Since spent reactor fuel which is a source of release of a neutron produces decay heat, if it is sealed for transportation or storage, it will generate heat, and serves as an elevated temperature. Although this maximum temperature changes with kinds of spent nuclear fuel, in the spent nuclear fuel corresponding to the degree of high combustion, it is said that the temperature within a cask reaches even near 200 **. Then, in order to use as a neutron shielding material, the thing

which is a storage rule of thumb of spent reactor fuel and which can be borne for about 60 years is desirable under such high temperature service.

[0004]For this reason, use of a substance with hydrogen density high as a shielding material, especially water is proposed, and practical use is also presented with the part. However, since water is a fluid, it is difficult handling and does not fit the cask especially aiming at transportation and storage. There is a problem that it is difficult to press down boil within the cask which amounts to not less than 100 **.

[0005]Conventionally, the resin composition was used as one material of a neutron shielding material, and the epoxy resin has been used for one of resin compositions. Generally, the hydrogen content of a resin composition and heat resistance are in reciprocity relation, and what has heat resistance low [what has many hydrogen contents] heat resistance and high has a hydrogen content in a low tendency. Although an epoxy resin is excellent in heat resistance or hardenability, since it was in the tendency little content of hydrogen indispensable in order to decelerate a neutron to be, its method of compensating this with the hardening agent of an amine system with many hydrogen contents was common.

[0006]While reducing viscosity and raising the workability in ordinary temperature using a polyfunctional amine system epoxy resin, the constituent for neutron shielding materials excellent in pot life is indicated by JP,6-148388,A. The neutron shielding material which made JP,9-176496,A harden the constituent which consists of an acrylic resin, an epoxy resin, silicone resin, etc. with the hardening agent of a polyamine system is indicated.

[0007]Since an amine compound has comparatively many hydrogen contents, the absorption effect of a neutron improves, but heat is easy to decompose combination of carbon and nitrogen which are contained in an amine system hardening agent. Therefore, development of the constituent which has endurance required in order to store and keep the spent reactor fuel corresponding to the degree of high combustion newer than the neutron shielding material which consists of resin hardened with the hardening agent of the conventional amine system is desired.

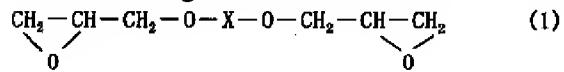
[0008]

[Problem(s) to be Solved by the Invention] An object of this invention is to provide the constituent for neutron shielding materials which heat endurance improved more and secured absorption of the neutron compared with the conventional constituent.

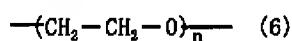
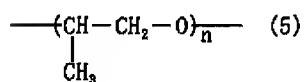
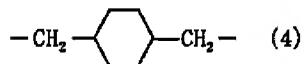
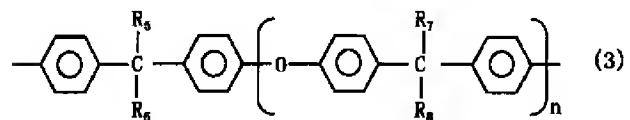
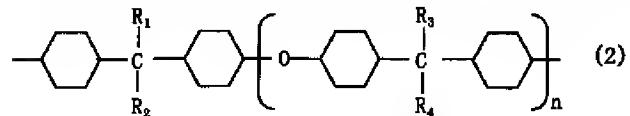
[0009]

[Means for Solving the Problem] This invention provides a constituent for neutron shielding materials containing a polymerization initiator, a polymerization component, and a boron compound. This invention provides a constituent for neutron shielding materials which does not contain a hardening agent. As a polymerization component, it is preferred that an epoxy ingredient is included. It is preferred as an epoxy ingredient that especially a hydrogenation

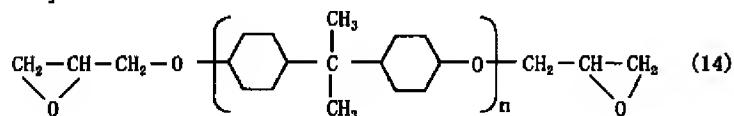
type epoxy compound is included. Here, the hydrogenation type epoxy compound refers to an epoxy compound of the benzene ring which maintained cyclic structure and raised content of hydrogen, although hydrogen is added in part at least and some conjugate states of the benzene ring are broken. This invention, [Formula 11]



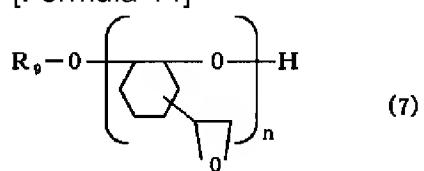
(The inside of a structural formula (1), and X) [Formula 12]



($R_1 - R_4$ among a structural formula (2)) It is independently chosen from the group which consists of CH_3 , H, F, Cl, and Br, respectively, are $n=0-2$, and $R_5 - R_8$ among a structural formula (3), It is independently chosen from the group which consists of CH_3 , H, F, Cl, and Br, respectively, either of being $n=0-2$, being $n=1-12$ among a structural formula (5), and being inside of a structural formula (6), and $n=1-24$, or one or more compounds in which C is chosen from the alkyl group of 1-20 -- it is -- containing is preferred. Said epoxy ingredient, [Formula 13]

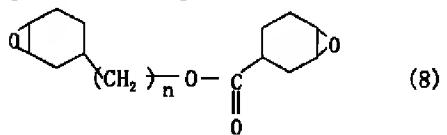


(structural-formula (14) It is preferred inside that $n=1-3$) are included. Said epoxy ingredient, [Formula 14]

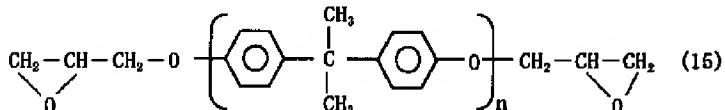


(structural-formula (7) C is an alkyl group of 1-10, or H, and inside and R₉ are with n= 1 - 24),

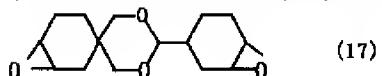
[Formula 15]



(structural-formula (8) The inside n= 1 - 8), [Formula 16]

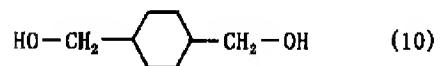
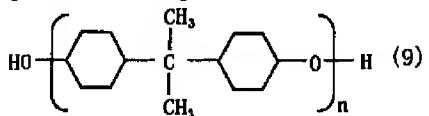


(structural-formula (15) The inside n= 1 - 3), [Formula 17]

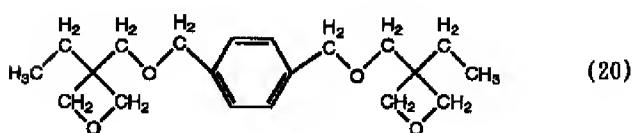
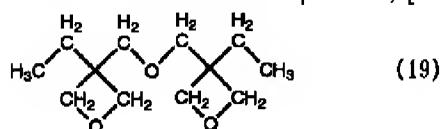


It is preferred that one or more compounds chosen from a group are included. As the compound to which it is preferred that a compound to which a hydrogen content of this constituent is made to increase is included further as for a constituent for neutron shielding materials of this invention, and said hydrogen content is made to increase furthermore,

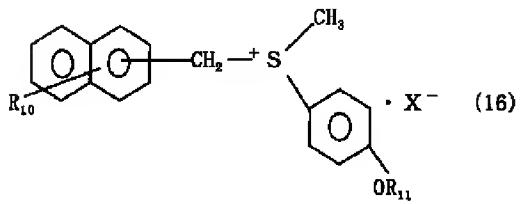
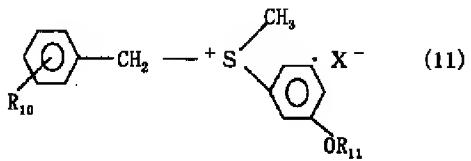
[Formula 18]



(structural-formula (9) It is preferred inside that at least one or more sorts of n= 1 - 3) are included. It is preferred that an oxetane compound is included as a polymerization component, and an oxetane compound, [Formula 19]



** -- it is preferred that at least one or more sorts are included among them. It is preferred that said polymerization initiator contains a cationic initiator, and said cationic initiator, [Formula 20]



(R₁₀ among a structural formula (11) and a structural formula (16)) they are a hydrogen atom, a halogen atom, a nitro group, and a methyl group -- R₁₁ -- a hydrogen atom, CH₃CO, CH₃OCO, and X -- SbF₆, PF₆, BF₄, and AsF₆ -- it is -- containing is preferred. It is preferred that a bulking agent is included further, it is preferred that a fire refractory material is included further, and it is preferred that said fire refractory material contains at least one or more sorts of magnesium hydroxide and aluminium hydroxide. This invention provides further a neutron shielding material and a neutron shield vessel which were manufactured with a constituent for neutron shielding materials. A compound to which the constituent of this invention can polymerize with a polymerization initiator, and since a reaction advances with an epoxy ingredient and a polymerization initiator preferably and a hardening agent of a weak amine system is not included in heat, a cask made from a constituent of this invention is that whose heat resistance improved. A hydrogen content in a constituent has also satisfied a reference value, and shielding performance of a neutron is also secured.

[0010]

[A mode of implementation of an invention] Below, a mode of operation of this invention is explained in detail. A mode of operation explained below does not limit this invention. A polymerization component means a compound which can polymerize with a polymerization initiator through this invention. In particular, in this invention, the following epoxy ingredients and oxetane ingredients are included as a polymerization component. An epoxy ingredient means a compound (henceforth an epoxy compound) which has an epoxy ring, and also when it is one kind of epoxy compound, and also when it is a mixture of two or more kinds of epoxy compounds, it contains. A compound which has an oxetane ring similarly is called oxetane compound, and also when it is one kind of oxetane compound, and also when it is a mixture of two or more kinds of oxetane compounds, it contains. A resinous principle means what set a thing which united the above polymerization components and a polymerization initiator ingredient and a compound which makes a hydrogen content increase to these, for example, diol etc.

[0011]In this invention, it makes it possible to make it harden without using a hardening agent which has a weak amine portion in heat a compound in which cationic polymerization is possible, and by adding a polymerization initiator ingredient to an epoxy compound, oxetane compounds, or those both especially. In order that the conventional constituent might use an amine compound for a hardening agent, heat-resistant resolvability under a high temperature state fell heat resistance, especially over a long period of time. In this invention, without using such a hardening agent, by making hardening possible, resin in which a connecting part of carbon and nitrogen which combination tends to disassemble by a high temperature state does not exist can be obtained, and big heat resistance can be expected. Therefore, since there is no heat-resistant fall accompanying hardening agent use like before, there is an advantage that character of requests, such as the amount of hydrogenation and heat resistance, can be added by selection of a polymerization component.

[0012]A constituent with high hydrogen content this invention is characterized by that comprises the following.

Polymerization component.

Polymerization initiator ingredient.

A boron compound which is a neutron absorption agent.

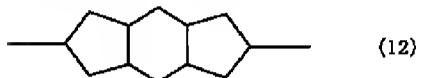
It is a constituent containing a fire refractory material, when it is made to harden and is considered as resin, it excels in heat resistance, and it is a high neutron shielding effect. Specifically, a constituent of this invention is asked for a hydrogen content preferably occupied to not less than 350 ** and the whole resinous principle being preferred, and not less than 330 ** of temperature of 90 % of the weight of weight survival rates by thermogravimetric analysis of a hardened material being 9.8 % of the weight or more still more preferably 9.0% of the weight or more. This is because reservation of a neutron shielding effect made into the purpose by adjustment of a fire refractory material fill ration, etc. is expectable, if a hydrogen content is 9.0 % of the weight or more.

[0013]It is so good that weight loss of a hardened material after heat durability under elevated-temperature sealing environment and a fall of compressive strength are small more particularly for a long period of time in addition to this, For example, it is called for that compressive strength is not falling 0.2 or less % of the weight preferably 0.5 or less % of the weight, or a rate of weight loss after sealing heat durability of $190^{\circ}\text{C} \times 1000\text{hr}$ is rising rather most preferably.

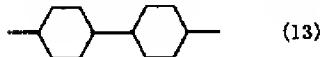
[0014]It is preferred to use a heat-resistant high compound for a polymerization component of this invention. Not less than 100 ** of epoxy compounds are preferably used from a viewpoint that heat resistance in near 200 ** is especially preferably required.

[0015]A compound which has an epoxy ring which can polymerize using a polymerization initiator ingredient of a cation system is used for an epoxy ingredient of this invention. In order

to raise heat resistance, it is preferred that crosslinking density of an epoxy ingredient is high. Since it will become a firm structure if many ring structures are included, heat resistance can be raised. The benzene ring is mentioned to a ring structure, for example. The benzene ring is upright, and although excelled in heat resistance, since there is little content of hydrogen with a role which slows down a neutron in this invention, a compound which carried out hydrogenation to the benzene ring is still more preferred. As a heat-resistant upright high structure, [Formula 21]



It comes out and the structure shown is preferred. Since it is preferred to contain more hydrogen, [Formula 22]



It comes out and the structure shown is the most preferred. The epoxy compound which has such a ring structure that added hydrogen to the benzene ring is called hydrogenation type epoxy compound through this specification. A hydrogenation type epoxy compound has an existing heat-resistant structure, and since hydrogen content is high, it is the most preferred as an epoxy compound of this invention.

[0016]An epoxy ingredient may mix two or more epoxy compounds [epoxy compound / one kind of]. An epoxy compound is chosen so that performance of requests, such as heat resistance and an increase in a hydrogen content, can be given.

[0017]quantity with a sufficient presentation of these epoxy ingredients for a hydrogen content of a resinous principle to cover a neutron -- it determines to become 9.8% of the weight or more still more preferably 9.0% of the weight or more preferably. Neutron shielding performance of a neutron shielding material is determined by a hydrogen content (density) of a neutron shielding material, and thickness of a neutron shielding material. This value based on a hydrogen content (density) required of a neutron shielding material determined from design thickness of a neutron shielding material of neutron shielding performance and a cask for which a cask is asked, It is based on a value which computed a hydrogen content for which a resinous principle is asked in consideration of loadings of a fire refractory material kneaded by neutron shielding material or a neutron absorber.

[0018]From such a viewpoint, it is a compound which carries out two or more owners of the epoxy ring preferably, and has a ring structure which is expressed with an upright structure, a structural formula (12), or a structural formula (13), and a compound with many hydrogen contents is suitable as an epoxy ingredient of this invention. Generally it is expressed with a structural formula (1) by such epoxy ingredient, and X in a formula, Structural formula (2) (R_1 ,

in a formula - R_4) Independently, it is chosen from CH_3 , H, F, Cl, and Br, and is a certain structural formula (3) (R_5 in a formula - R_8) at $n= 0-2$, respectively. It is independently chosen from CH_3 , H, F, Cl, and Br, respectively, and is $n= 0-2$ -- it is preferred to be chosen from a structural formula (4), a structural formula (5), (the inside of a formula and $n= 1-12$), and the structural formula (6), and (the inside of a formula and $n= 1-24$).

[0019]Especially, hydrogenation bisphenol A type epoxy expressed with a structural formula (14) is used as a most suitable and important epoxy ingredient from balance of a hydrogen content and heat resistance.

[0020]As an ingredient for furthermore giving heat resistance, bisphenol A type epoxy (structural formula (15)) can be added. It is because it has the benzene ring and has an upright structure. a structural formula (7) from a viewpoint that crosslinking density is high and heat resistance is good -- (among a formula, C is an alkyl group of 1-10, or H, and, as for R₉, it is preferred to add n= 1 - 24), a structural formula (8), (the inside of a formula and n= 1-8), or a structural formula (17).

[0021]Therefore, it becomes possible to consider it as a constituent which has a desired hydrogen content and heat resistance by mixing and using at least one or more compounds chosen from a group which becomes a structural formula (14) from a structural formula (15), a structural formula (7), a structural formula (8), and a structural formula (17), for example.

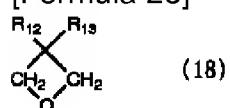
Therefore, an epoxy ingredient of this invention contains an epoxy compound shown with a structural formula (14), further, may also contain a structural formula (15), structural formulae (7), structural formulae (8), and all the structural formulae (17), and may also include a part of them. All the combination considered using these epoxy compounds is possible.

[0022]In this case, it is preferred that hydrogenation bisphenol A type epoxy of a structural formula (14) is included 70% of the weight or more to the whole resinous principle, As for screw A type epoxy of a structural formula (15), it is preferred that a structural formula (8) contains a structural formula (7) at 30 or less % of the weight, and is included at 25 or less % of the weight, and a structural formula (17) is included in 30 or less % of the weight of quantity 20 or less % of the weight.

[0023]From a viewpoint of increasing especially the amount of hydrogenation, an oxetane compound can be used as a polymerization component. Cationic polymerization is possible for an oxetane compound like epoxy, and it is abundant in hydrogen contents, and heat resistance can also expect it to some extent.

[0024] An oxetane compound is generally a structural formula (18).

[Formula 23]



(-- a structural formula -- (-- 18 --) -- inside -- R -- ₁₂ -- R -- ₁₃ -- respectively -- independently -- H -- halogen -- C -- one - eight -- alkyl -- alcohol -- others -- carbon -- hydrogen -- oxygen -- from -- becoming -- an organic compound -- containing -- structure -- it is --) -- expressing -- having . The oxetane compound used by this invention may be a compound which has two or more oxetane rings via an ether bond or the benzene ring.

[0025] Specifically as an oxetane compound used for this invention, a structural formula (19) and a structural formula (20) are preferred. A compound which has at least two or more oxetane rings, for example via an ether bond, a ring structure, etc. is preferred like a structural formula (19) instead of what is limited to these. It is because heat-resistant grant by improvement in crosslinking density is expectable by many oxetane rings being included. Since a constituent of this invention is especially asked for heat-resistant grant, to it, an oxetane compound which has many ring structures, much branching structure, etc. is preferred.

[0026] An oxetane ingredient can also be independently used as a polymerization component, without using an epoxy compound. Two or more oxetane compounds can also be used. It can use as a polymerization component used together with arbitrary epoxy ingredients. For example, as a combination of a desirable polymerization component, It is possible to use an oxetane ingredient of a structural formula (19), an epoxy ingredient of a structural formula (7) and an oxetane ingredient of a structural formula (19), an epoxy ingredient of a structural formula (8) and an oxetane ingredient of a structural formula (19), an epoxy ingredient of a structural formula (17), etc.

[0027] As an example of composition ratio of a polymerization component using an oxetane compound, what contains 85.5 % of the weight and a structural formula (15) 14.5% is mentioned in a structural formula (19). Or what contains 20.0 % of the weight and a structural formula (7) 6.0% is mentioned [structural formula / 74.0 % of the weight and / (20)] in a structural formula (19).

[0028] Although it is classified into a radical system, an anionic system, a cation system, etc. and a large number are reported by literature etc. as a polymerization initiator, respectively, in this invention, a polymerization initiator of a cation system is used preferably. An example of a thing prominent as a polymerization initiator of a cation system is shown in Table 1. As a cation system thermal polymerization initiator which can make a polymerization start with heat, OPUTON CP series of Asahi Denka Kogyo K.K., SI series of 3 Japanese Federation of Chemical Industry Workers' Unions, Inc., and DAICAT EX-1 grade of Daicel Chemical Industries, Ltd. are mentioned. Although it is possible to use these polymerization initiators in this invention, it is not limited to them.

[0029]

[Table 1]

一般的な重合開始剤成分

構造	商品名	供給元	
	X=SbF6 UVI-6974	UCC	
	X=PF6 UVI-6990	UCC	
	X=SbF6 UVI-6970 (SP-170)	X=PF6 UVI-6950 (SP-150)	旭電化
	Degacure K126	Degussa	
	FX-512	3M	
	X=SbF6 PIC-061T	X=PF6 PIC-062T	日本化薬
	X=SbF6 PIC-020T	X=PF6 PIC-022T	日本化薬
	合成スルホニウム塩	日本曹達	
	UV-9380C	GE	
	IOC-10	GE	
	CD-1012	Sartomer	
	2074	Rhône-Poulenc Chimie	
	Irga-cure 261	Chiba-Geigy	
		東芝	

[0030]As a polymerization initiator, a compound shown with a structural formula (11) or a structural formula (16) is added preferably. When the whole resinous principle is made into 100 weight sections, as for a polymerization initiator, it is preferred to add by 0.5 to 6 weight

section, and it is still more preferred to add by one to 3 weight section. It is because there is a possibility of making a hydrogen content to the whole constituent falling when it adds too much not much mostly.

[0031]In order to make a hydrogen content increase to the constituent of this invention, it is a compound which does not have an epoxy ring and it is also possible to add the compound containing many hydrogen. Since there is a limit in increasing a hydrogen content only with an epoxy compound, these compounds can be added in option, when hydrogen contents run short. At this time, it is necessary to choose a compound so that the compound to add may not change the physical properties of the whole system of a constituent a lot. For example, since the polymerization reaction of an epoxy ingredient will not advance to it if the compound of an amine system is mixed to the constituent containing the polymerization initiator of a cation system of this invention, an amine compound cannot be added to it. As a result of inquiring in consideration of such a point, as a compound for making a hydrogen content increase, diol is suitable, for example.

[0032]Although it can apply if an epoxy ingredient and a polymerization are possible meltable to an epoxy ingredient, and aliphatic series diol, aromaticdiol, the diol that has fat ring structure, polyol, etc. can be used as diol, it is not limited to these. From the increase in a hydrogen content, and a point of control of a heat-resistant fall, the compound expressed with the diol which has fat ring structure preferably, for example, a structural formula, (9), and a structural formula (10) is used. As for the addition of diol, it is preferred that it is 30 or less % of the weight to the whole resinous principle, and it is still more preferred that it is 20 or less % of the weight.

[0033]It is also possible to use the alcohols of the polyfunctional mold of three or more organic functions, etc. as a thing which is not limited to diol but can expect the same effect as the oxetane and vinyl ether in which cation hardening is possible, and diol as a compound for making the hydrogen content of a constituent increase.

[0034]Although boron carbide, boron nitride, anhydrous boric acid, boron iron, an ashes Howe stone, orthoboric acid, metaboric acid, etc. are among the boron compounds used as a neutron absorption agent of the constituent of this invention, boron carbide is the most preferred in respect of neutron shielding performance.

[0035]Although powder is used as for the above-mentioned boron compound, there is no restriction in particular in the particle size and addition. However, if the dispersibility in the epoxy resin of matrix resin and the cover nature to a neutron are taken into consideration, about 1-200 microns of mean particle diameter are preferred, its about 10-100 microns are more preferred, and especially its about 20-50 microns are preferred. On the other hand, 0.5 thru/or 20% of the weight of the range of an addition is the most preferred to the whole constituent also including the below-mentioned bulking agent. At less than 0.5 % of the weight,

when the effect as a neutron shielding material of the added boron compound is low and exceeds 20 % of the weight, it becomes difficult to distribute a boron compound uniformly. [0036]Glass fiber besides powder, such as silica, alumina, calcium carbonate, antimonous oxide, titanium oxide, asbestos, clay, and mica, etc. is used for this invention as a bulking agent, and carbon fiber etc. may be added if needed. If needed Natural wax as a release agent, metal salt of fatty acid, The chloroparaffin as fire retardant, such as acid amides and fatty acid ester, bromine toluene, hexa bromobenzene, antimonous oxide, etc. can add the others, a silane coupling agent, a titanium coupling agent, etc. which are carbon black as colorant, red ochre, etc.

[0037]Even when a fire is encountered, the fire-resistant agent used in the constituent concerning this invention should aim at making a neutron shielding material remain above to some extent so that the above neutron shield capability can be maintained to some extent. Especially as such a fire refractory material, it is preferred to use magnesium hydroxide and aluminium hydroxide. Especially, since magnesium hydroxide exists stably also at nearly 200 elevated temperatures, it is especially preferred. As for the addition of these fire-resistant agent, 20 to 70 % of the weight is preferred among the above-mentioned whole constituent, and especially its 35 to 60 % of the weight is preferred.

[0038]The constituent of this invention is adjusted by adding a polymerization initiator at the last, after carrying out after mixing a polymerization component, for example, an epoxy ingredient, and other additive agents, preparing a resin composition and kneading this, a fire refractory material, a neutron absorber, etc. As polymerization conditions, although it changes also with presentations of a resinous principle, on temperature conditions (50 ** - 200 **), it is preferred to perform heating for 1 hour - 3 hours. It is preferred to perform such heat-treatment in two steps, after heating at 80 ** - 120 ** for 1 hour - 2 hours, it is 120 ** - 180 **, and it is preferred to heat-treat from 2 hours for 3 hours, but it is not limited to this, such as a preparing method and curing conditions.

[0039]the container for covering the neutron of spent reactor fuel effectively and doing storage and transportation of it -- a cask can be manufactured preferably. Such a cask for transportation can be manufactured using known art. For example, the part filled up with a neutron shield is established in the cask indicated by JP,2000-9890,A. Such a part can be filled up with the constituent of this invention.

[0040]Without being limited to the screen in such a cask, in the device and institution which prevent diffusion of a neutron, the constituent of this invention can be used for various parts, and can cover a neutron effectively.

[0041]

[Example]An example is used for below and this invention is explained to it in detail. The following examples do not limit this invention.

[0042]In the example, the constituent of this invention was prepared and the neutron shielding effect was investigated. Usually, to the resin composition for neutron shielding materials, boron compounds, such as boron carbide, are mixed for aluminium hydroxide, magnesium hydroxide, etc. as a fire refractory material, about 1% of the weight of the whole is mixed as about 60 whole % of the weight and neutron absorption agent, and a neutron shielding material is produced to it. However, the fire refractory material and the neutron absorption agent centered on what is not added here that the performance by a resinous principle, i.e., a polymerization component, a polymerization initiator ingredient, etc., should be evaluated.

[0043]As performance for which a neutron shielding material is asked, there are heat resistance (a weight survival rate, compressive strength, etc.), refractoriness, a hydrogen content (a certain thing is [more than constant rate that has the hydrogen content density in material as a judgment rule of thumb of the fitness as neutron cover] needed), etc. Since the portion by a fire refractory material was size, refractoriness evaluated the heat resistance and the hydrogen content which are seen to a weight survival rate as evaluation of the resin composition for neutron shielding materials. A weight survival rate evaluates the heat resistance by measuring the weight change at the time of temperature up. For measurement, the measuring condition of thermo gravity reduction measured even room temperature -600 ** under the heating rate of 10 ** / min, and a nitrogen atmosphere using TGA. As a reference value of the hydrogen content for which resin is asked, the hydrogen content in the inside of a resin simple substance was made into about 9.8 % of the weight or more.

[0044][Example 1] -- as an epoxy resin -- a hydrogenation bisphenol A type epoxy resin (the product made from Oil recovery Shell Epoxy.) It was considered as the resin composition which is stirred well and used for neutron shielding materials until it added cation system polymerization initiator SI-80 [1g] (structural formula (11)) in YL6663 and 100 g of structural formulae (14) and the polymerization initiator dissolved in them. As a result of measuring the hydrogen content of the above-mentioned resin composition for neutron shielding materials, the hydrogen content was satisfied with 9.8 % of the weight or more (about 10 % of the weight or more) of the reference value. Next, the constituent was stiffened by 80 **x30min+150 **x2hr, and thermo gravity reduction of the hardened material was measured by TGA. The measuring condition of thermo gravity reduction measured even RT-600 ** under the heating rate of 10 ** / min, and a nitrogen atmosphere. The temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 350 **, very good heat resistance, and thermal stability as a result of measurement.

[0045][Example 2] As an epoxy resin, 84.6 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), Cation system polymerization initiator SI-80 [1g] (structural formula (11)) is added to what mixed 15.4 g of bisphenol A type epoxy resins (the product

made from Oil recovery Shell Epoxy, Epicoat 828, structural formula (15)), It was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition by the same method as Example 1, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 380 **, very good heat resistance, and thermal stability.

[0046][Example 3] As an epoxy resin, 74.8 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), 25.2 g of polyfunctional alicycle type epoxy resins (the product made from Die Cell Chemicals, EHPE3150, structural formula (7)) were mixed, and it stirred well until it held at 110 ** and EHPE3150 (solid) dissolved. It was neglected to the room temperature after the EHPE3150 dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of about 99.5 % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 390 **, very good heat resistance, and thermal stability.

[0047][Example 4] As an epoxy resin, 79.4 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), Cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added to what mixed 20.6 g of alicycle type epoxy resins (the product made from Die Cell Chemicals, the SEROKI side 2021P, a structural formula (8)), and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 370 **, very good heat resistance, and thermal stability.

[0048][Example 5] As an epoxy resin, 8.23 g of hydrogenation bisphenol A type epoxy resins

(YL6663, structural formula (14)), and 8.85 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)), Cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added to what mixed 8.85 g of alicycle type epoxy resins (the SEROKI side 2021P, a structural formula (8)), and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 380 **, very good heat resistance, and thermal stability.

[0049][Example 6] as an epoxy resin. 80.9 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), 9.55 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)), and 9.55 g of polyfunctional alicycle type epoxy resins (EHPE3150, structural formula (7)) are mixed, It stirred well until it held at 110 ** and EHPE3150 (solid) dissolved. It was neglected to the room temperature after the EHPE3150 dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 390 **, very good heat resistance, and thermal stability.

[0050][Example 7] -- as an epoxy resin -- 77.3 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), and an alicycle type epoxy resin (the SEROKI side 2021P.) 11.35 g of polyfunctional alicycle type epoxy resins (EHPE3150, structural formula (7)) were mixed with 11.35 g of structural formulae (8), and it stirred well until it held at 110 ** and EHPE3150 (solid) dissolved. It was neglected to the room temperature after the EHPE3150 dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the

reference value. As a result of stiffening the above-mentioned resin composition for neutron shielding materials by 80 **x30min+150 **x2hr and measuring thermo gravity reduction on the other hand, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 390 **, very good heat resistance, and thermal stability.

[0051][Example 8] -- as an epoxy resin -- 80.38 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), and 6.54 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)) and an alicycle type epoxy resin (the SEROKI side 2021P.) 6.54 g of polyfunctional alicycle type epoxy resins (EHPE3150, structural formula (7)) were mixed with 6.54 g of structural formulae (8), and it stirred well until it held at 110 ** and EHPE3150 (solid) dissolved. It was neglected to the room temperature after the EHPE3150 dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 400 **, very good heat resistance, and thermal stability.

[0052][Example 9] As an epoxy resin, 63.8 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), It stirred well until it mixed 10 g, it held 26.2 g of alicycle type epoxy resins (the SEROKI side 2021P, a structural formula (8)), and a hydrogenation bisphenol (the New Japan Chemical Co., Ltd. make, Rika Vinol HB, structural formula (9)) at 100 ** and Rika Vinol HB (solid) dissolved. It was neglected to the room temperature after the Rika Vinol HB dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of about 99.5 % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 380 **, very good heat resistance, and thermal stability.

[0053][Example 10] As an epoxy resin, 66.1 g of hydrogenation bisphenol A type epoxy resins

(YL6663, structural formula (14)), and 23.9 g of alicycle type epoxy resins (the SEROKI side 2021P, a structural formula (8)), 10 g of cyclohexane dimethanol (the Tokyo Kasei Kogyo Co., Ltd. make, structural formula (10)) was mixed, and it stirred well until it held at 100 ** and cyclohexane dimethanol (the shape of a wax) dissolved. It was neglected to the room temperature after the cyclohexane dimethanol dissolution, when temperature fell to near a room temperature, cation system polymerization initiator SI-80 [1g] (structural formula (11)) was added, and it was considered as the resin composition which is stirred well and used for neutron shielding materials until the polymerization initiator dissolved. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with about 9.8 % of the weight of the reference value. As a result of stiffening the above-mentioned resin composition for neutron shielding materials by 80 **x30min+150 **x2hr and measuring thermo gravity reduction on the other hand, the temperature of about 99.5 % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 380 **, very good heat resistance, and thermal stability.

[0054][Example 11] Here, the neutron shielding material which mixed further the neutron absorption agent and the fire refractory material was evaluated. as an epoxy resin -- 80.38 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), and 6.54 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)) and an alicycle type epoxy resin (the SEROKI side 2021P.) 6.54 g of polyfunctional alicycle type epoxy resins (EHPE3150, structural formula (7)) were mixed with 6.54 g of structural formulae (8), and it stirred well until it held at 110 ** and EHPE3150 (solid) dissolved. After the EHPE3150 dissolution, 146.5 g and 3.5 g of boron carbide were mixed and stirred, and 170 **x2hr maintenance of the magnesium hydroxide was carried out. When it allowed to stand at the room temperature after 170 **x2hr maintenance and the temperature of the mixture turned into a room temperature grade, 2g was easy to add, cation system polymerization initiator SI-80 (structural formula (11)) was stirred, and it was considered as the constituent for neutron shielding materials. As a rule of thumb of the hydrogen content for which a neutron shielding material is asked, hydrogen content density is more than 0.096 g/cm³. As a result of measuring the hydrogen content density of the prepared neutron shielding material constituent, the reference value was satisfied above 0.096 g/cm³. The hydrogen content in the resinous principle measured separately was 9.8 % of the weight or more. On the other hand, the above-mentioned resin composition for neutron shielding materials was stiffened by 170 **x4hr, and as a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 % of the weight or more of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 400 **, very good heat resistance, and thermal stability. The heat-resistant durability test of 190 **x1000hr was done after sealing the above-mentioned hardened material hermetically in a well-closed container. Compressive

strength rose by 1.4 or more times compared with examination before, and showed the endurance whose rate of weight loss is also very good at about 0.1%.

[0055][Example 12] -- as an epoxy resin -- 63.8 g of hydrogenation bisphenol A type epoxy resins (YL6663, structural formula (14)), and an alicycle type epoxy resin (the SEROKI side 2021P.) 10 g of hydrogenation bisphenols (Rika Vinol HB, structural formula (9)) were mixed with 26.2 g of structural formulae (8), and it stirred well until it held at 100 ** and Rika Vinol HB (solid) dissolved. After the Rika Vinol HB dissolution, 146.5 g and 3.5 g of boron carbide were mixed and stirred, and 170 **x2hr maintenance of the magnesium hydroxide was carried out. When it allowed to stand at the room temperature after 170 **x2hr maintenance and the temperature of the mixture turned into a room temperature grade, 2g was easy to add, cation system polymerization initiator SI-80L (structural formula (11)) was stirred, and it was considered as the constituent for neutron shielding materials. As a rule of thumb of the hydrogen content for which a neutron shielding material is asked, although hydrogen content density was more than 0.096 g/cm³, as a result of measuring the hydrogen content density of the prepared neutron shielding material constituent, the reference value was satisfied above 0.096 g/cm³. As a result of stiffening the above-mentioned resin composition for neutron shielding materials by 170 **x4hr and measuring thermo gravity reduction on the other hand, the temperature of about 99.5 % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates showed not less than 380 **, very good heat resistance, and thermal stability. The heat-resistant durability test of 200 **x500hr was done after sealing the above-mentioned hardened material hermetically in a well-closed container. Compressive strength rose by 1.2 or more times compared with examination before, and showed the endurance whose rate of weight loss is also very good at about 0.1%.

[0056]Next, as a comparative example, the performance of the neutron shielding material by the constituent used from the former was evaluated. The fire refractory material and the neutron absorption agent were not added like the example. The hydrogen content asked for thermo gravity reduction by measuring by TGA by component analysis like the example.

[0057][Comparative example 1] 82.5 g of hydrogenation bisphenol A type epoxy resins (Oil recovery Shell Epoxy, YL6663) shown with the structural formula (14) same as an epoxy resin as Example 1, It was considered as the resin composition which stirs 17.5 g of isophoronediamine well as a hardening agent, and is used for neutron shielding materials. This shows the comparative example of the neutron shielding material using the hardening agent in comparison with this invention. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with 9.8 % of the weight or more of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of about 99.5 % of the

weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates is about 300 **, and heat resistance and thermal stability were inferior as compared with a group of an example. It differs greatly in that this presentation system uses an amine system hardening agent instead of a cation system polymerization initiator as compared with Example 1. It turns out that heat resistance and thermal stability improve by making it harden with a polymerization initiator like Example 1 from comparison with Example 1 and the comparative example 1.

[0058][Comparative example 2] It was considered as 81.4 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)), and the resin composition which stirs 18.6 g of isophoronediamine well as hardening agents, and is used for neutron shielding materials as an epoxy resin. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was much less than the reference value at 8.2 or less % of the weight, and became in transit. As a result of stiffening the above-mentioned resin composition for neutron shielding materials by 80 **x30min+150 **x2hr and measuring thermo gravity reduction by the same method as Example 1 on the other hand, about 350 **, heat resistance, and thermal stability had a good temperature of about 99.5 % of the weight of weight survival rates in 200 **, and 90 % of the weight of weight survival rates. Although this presentation system was good on heat resistance and a thermal stability target, it was unsuitable as a resin composition for neutron shielding materials from a point of a hydrogen content. It differs greatly in that this presentation system uses an amine system hardening agent instead of a cation system polymerization initiator as compared with the comparative example 2. Comparison of the comparative example 2 and the comparative example 3 also shows that heat resistance and thermal stability improve by making it harden with a polymerization initiator.

[0059][Comparative example 3] It was considered as the resin composition which mixes and stirs a bisphenol A type epoxy resin (Epicoat 828, structural formula (15)) and the hardening agent of a polyamine system at a rate of 1:1 (it becomes an equivalent amount stoichiometrically) as an epoxy resin, and is used for neutron shielding materials. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with 9.8 % of the weight or more of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99 or less % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates is 300 ** or less, and heat resistance and thermal stability were inferior as compared with a group of an example. Although this presentation system imitated the same system as the resin composition for neutron shielding materials currently used from the former, Although the comparative example 4 has fitness from a point of a hydrogen content, as compared with a group of an example, it is a low value, and a group of an example

is known by heat resistance and excelling in thermal stability at heat resistance and a thermal stability target.

[0060][Comparative example 4] 81.7 g of epoxy resins (epoxy equivalent weight 190) with the structure which replaced OH of the both ends of a polypropylene glycol by glycidyl ether as an epoxy resin, respectively, It was considered as the resin composition which stirs 18.3 g of isophoronediamine well as a hardening agent, and is used for neutron shielding materials. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with 9.8 % of the weight or more of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80

**x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 or less % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates is less than about 250 **, and heat resistance and thermal stability were extremely inferior as compared with a group of an example.

[0061][Comparative example 5] It was considered as 1, 78.5 g of 6 hexane diglycidyl ether (epoxy equivalent weight 155), and the resin composition that stirs 21.5 g of isophoronediamine well as hardening agents, and is used for neutron shielding materials as an epoxy resin. As a result of measuring the hydrogen content in a resin composition, the hydrogen content was satisfied with 9.8 % of the weight or more of the reference value. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99.5 or less % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates is less than 300 **, and heat resistance and thermal stability were inferior as compared with a group of an example.

[0062][Comparative example 6] Here, the neutron absorption agent was added to the resinous principle of the conventional type, and the neutron shielding effect was evaluated. 146.5 g and 3.5 g of boron carbide were mixed and stirred, and magnesium hydroxide was used as the constituent for neutron shielding materials what mixed and stirred 50 g of bisphenol A type epoxy resins (Epicoat 828, structural formula (15)), and the hardening agent 50g of a polyamine system as an epoxy resin. As a rule of thumb of the hydrogen content for which a neutron shielding material is asked, although hydrogen content density was more than 0.096 g/cm³, as a result of measuring the hydrogen content density of the prepared neutron shielding material constituent, the reference value was satisfied above 0.096 g/cm³. On the other hand, the above-mentioned resin composition for neutron shielding materials is stiffened by 80 **x30min+150 **x2hr, As a result of measuring thermo gravity reduction by the same method as Example 1, the temperature of 99 or less % of the weight of weight survival rates in 200 ** and 90 % of the weight of weight survival rates is 300 ** or less, and heat resistance and thermal stability were inferior as compared with a group of an example. The heat-resistant

durability test of 190 **x1000hr was done after sealing the above-mentioned hardened material hermetically in a well-closed container. Compressive strength fell 30 percent or more compared with examination before, and the endurance under hot environments became low. Although this presentation system imitated the same system as the constituent for neutron shielding materials currently used from the former, Although the comparative example 6 has fitness from a point of a hydrogen content, as compared with Example 11 and Example 12, it is a low value, and an example is known by heat resistance and excelling in thermal stability at heat resistance and a thermal stability target.

[0063]When the same polymerization component compared from the above example and a comparative example, compared with the resin hardened with the amine system hardening agent, it turned out that the temperature at the 90 % of the weight of weight survival-rates time rises by 30-50 ** on the average, and has become a heat-resistant high thing by the resin hardened with the polymerization initiator of this invention.

[0064]

[Effect of the Invention]The neutron shielding material obtained with the constituent for neutron shielding materials of this invention stiffens the existing heat-resistant polymerization component using a cation system polymerization initiator. Without using the hardening agent component which has combination which is easy to decompose under high temperature service, heat-resistant temperature rises and the constituent of this invention which can polymerize also secures a neutron shielding effect, when it hardens and is made into a shielding agent. Therefore, this invention can provide the constituent for neutron shielding materials which can be equal also to the storage over the long period of time of spent reactor fuel.

[Translation done.]